Structural characterization of a cationic zirconocene olefin polymerization catalyst with its methylated boralumoxane counterion

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"First structural characterization of a cationic zirconocene olefin polymerization catalyst with its methylated alumoxane counterion"

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General:

All experiments were performed under nitrogen atmosphere using standard Schenk and glove box techniques. Toluene, pentane and hexanes (Aldrich anhydrous) were passed under nitrogen atmosphere over columns of molecular sieves (4Å) before use. [D_6]benzene (Aldrich) was vacuum transferred from Na/K alloy. [D_5]bromobenzene (Aldrich) was degassed and dried over molecular sieves (4Å). [*t*$Bu_4Al_4Ar_4B_4O_8$] (**1**) was prepared as reported previously (ref. 7 in the paper). Allyl-methyl-thioether (3-methylthio-1-propene, Janssen) was distilled from sodium. Pyridine and 2,6-dimethylpyridine (Aldrich) were distilled from KOH. $Cp^*_2ZrMe_2$ was prepared according to literature procedures (Manriquez et al. *J. Am. Chem. Soc.* 100 (1978) 2716). NMR spectra were recorded on a Varian Unity 500 instrument, at 500 MHz (^{1}H), 125.7 MHz (^{13}C), 160,4 MHz (^{11}B), 130.3 MHz (^{27}Al) and at 25 °C. Spectra were referenced to resonances of the solvent (^{1}H, ^{13}C) or external standards $BF_3(Et_2O)$ (^{11}B), $Al(NO_3)_3/D_2O$ (^{27}Al).

Synthesis of $Al(Bu^t_2Al)(Bu^tAl)_2(O_2BAr)_4(C_5H_5N)$ (**2**):

Pyridine (26.5 µl, 0.328 mmol) was added to a suspension of **1** (0.378 g, 0.328 mmol) in 5 ml of *n*-pentane. Subsequently 3 ml of toluene was added, and the mixture was briefly warmed to 40°C. After allowing the mixture to cool to ambient temperature, the supernatant was decanted and the precipitate was rinsed with 5 ml of *n*-hexane. Drying in vacuo yielded **2** (0.240 g, 59%).

$Al(Bu^t_2Al)(Bu^tAl)_2(O_2BAr)_4(C_5H_6N)$ (**2**): Elemental analysis for $C_{69}H_{109}NO_8B_4Al_4$ (1231.8) found (calcd): %C = 67.22 (67.28), %H = 8.88 (8.92), N% = 1.07 (1.14). ^{1}H-NMR (500 MHz, [D_6]benzene, 25^{o}C): δ = 7.52 (d, ^3J(H,H) = 5.0 Hz, 2 H; *o*-Py*H*), 7.46 (t, ^3J(H,H) = 7.0 Hz, 1 H; *p*-Ar*H*), 7.36 (br, 1 H, *p*-Ar*H*), 7.28, (t, ^3J(H,H) = 7.0 Hz, 1 H; *p*-Ar*H*), 7.27 (t, ^3J(H,H) = 7.5 Hz, 1 H; *p*-Ar*H*), 7.21 (d , ^3J(H,H) = 8.0 Hz, 2 H; *m*-Ar*H*), 7.17 (m, 2 H; *m*-Ar*H*), 7.12 (m, 2 H; *m*-Ar*H*), 7.06 (d, ^3J(H,H) = 7.0 Hz, 1 H; *m*-Ar*H*), 6.93 (d, ^3J(H,H) = 8.0 Hz, 1 H; *m*-Ar*H*), 6.79 (t, ^3J(H,H) = 7.7 Hz, 1 H; *p*-Py*H*), 6.40 (t, ^3J(H,H) = 6.7 Hz, 2 H; *m*-Py*H*), 4.08 (sept, ^3J(H,H) = 6.5 Hz, 1 H; C*H*$(CH_3)_2$), 3.51 (br, 2 H, C*H*$(CH_3)_2$), 3.47 (sept, ^3J(H,H) = 6.5 Hz, 1 H; C*H*$(CH_3)_2$), 3.37 (sept, ^3J(H,H) = 7.0 Hz, 2 H; C*H*$(CH_3)_2$), 3.14 (sept, ^3J(H,H) = 7.0 Hz, 1 H; C*H*$(CH_3)_2$), 2.84 (sept, ^3J(H,H) = 6.5 Hz, 1 H; C*H*$(CH_3)_2$), 1.65 (m, 6 H; CH(C*H*$_3)_2$), 1.62 (br, 12 H; CH(C*H*$_3)_2$), 1.55 (d, ^3J(H,H) = 6.5 Hz, 3 H; CH(C*H*$_3)_2$), 1.51 (d, ^3J(H,H) = 6.0 Hz, 3 H; CH(C*H*$_3)_2$), 1.50 (d, ^3J(H,H) = 6.5 Hz, 3 H; CH(C*H*$_3)_2$), 1.40 (d, ^3J(H,H) = 6.5 Hz, 3 H; CH(C*H*$_3)_2$), 1.37 (d, ^3J(H,H) = 7.0 Hz, 3 H; CH(C*H*$_3)_2$), 1.35 (d, ^3J(H,H) = 7.0 Hz, 3 H, CH(C*H*$_3)_2$), 1.26 (s, 9 H; C(C*H*$_3)_3$), 1.23 (d, ^3J(H,H) = 7.0 Hz, 3 H; CH(C*H*$_3)_2$), 1.18 (d, ^3J(H,H) = 6.5 Hz, 3 H; CH(C*H*$_3)_2$), 1.02 (d, ^3J(H,H) = 6.0 Hz, 3 H; CH(C*H*$_3)_2$), 0.96 (s, 9 H; C(C*H*$_3)_3$), 0.83 (s, 9 H; C(C*H*$_3)_3$), 0.75 (s, 9 H; C(C*H*$_3)_3$), 0.39 (d, ^3J(H,H) = 6.5 Hz, 3 H; CH(C*H*$_3)_2$). ^{13}C NMR (126 MHz, [D_6]benzene, 25^{o}C): δ = 154.3 (*o*-Ar*C*), 153.0 (*o*-Ar*C*), 152.9 (*o*-Ar*C*), 151.9 (*o*-Ar*C*), 147.6 (*o*-Ar*C*), 147.3 (*o*-Py*C*), 143.1 (*p*-Py*C*), 131.0 (*p*-Ar*C*), 130.0 (*p*-Ar*C*), 129.4 (*p*-Ar*C*), 127.3 (*p*-Ar*C*), 125.7 (*m*-Py*C*), 122.7 (*m*-Ar*C*), 122.2 (*m*-Ar*C*), 121.9 (*m*-Ar*C*), 120.9 (*m*-Ar*C*), 36.3 (*C*H$(CH_3)_2$), 36.2 (*C*H$(CH_3)_2$), 36.1 (*C*H$(CH_3)_2$), 36.0 (*C*H$(CH_3)_2$), 35.8 (*C*H$(CH_3)_2$), 35.7 (*C*H$(CH_3)_2$), 35.3 (*C*H$(CH_3)_2$), 35.1 (*C*H$(CH_3)_2$), 32.3 (CH(*C*H$_3)_2$), 31.9 (CH(*C*H$_3)_2$), 31.8 (CH(*C*H$_3)_2$), 31.7 (C(*C*H$_3)_3$), 31.3 (CH(*C*H$_3)_2$), 31.1 (C(*C*H$_3)_3$), 30.4 (CH(*C*H$_3)_2$), 30.2 (CH(*C*H$_3)_2$), 30.1 (C(*C*H$_3)_3$), 30.0 (CH(*C*H$_3)_2$), 29.8 (C(*C*H$_3)_3$), 29.6 (CH(*C*H$_3)_2$), 29.3 (CH(*C*H$_3)_2$), 28.2 (CH(*C*H$_3)_2$), 27.7 (CH(*C*H$_3)_2$), 23.4 (CH(*C*H$_3)_2$), 23.1 (CH(*C*H$_3)_2$), 21.7 (CH(*C*H$_3)_2$), 21.4 (CH(*C*H$_3)_2$), 21.3 (CH(*C*H$_3)_2$), 21.0 (CH(*C*H$_3)_2$). ^{11}B NMR (160 MHz, [D_6]benzene, 25^{o}C): δ = 30.0 ($W_{1/2}$ = 2640 Hz). ^{27}Al (130 MHz, [D_6]benzene, 25^{o}C): δ = 120 (very br, $W_{1/2}$ > 50 kHz), 41.9 ($W_{1/2}$ = 5900 Hz).

Single crystals of **2**.(benzene) were obtained by performing the reaction between **1** and pyridine on 50 μmol scale in 0.8 ml of benzene at ambient temperature and concentrating the solution to half the volume. Allowing this solution to stand at ambient temperature resulted in the gradual separation of crystals of **2**.(benzene) suitable for X-ray diffraction.

Synthesis of $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2SMe]\text{-}[Al(Bu^t_2Al)(Bu^tAl)(Bu^tAlMe)(O_2BAr)_4].(C_7H_8)_{1.5}$ (**3**)

A solution of $Cp^*_2ZrMe_2$ (0.134 g, 0.343 mmol) in 2 ml of toluene was added to a suspension of **1** (0.368 g, 0.319 mmol) in 3 ml of *n*-pentane. Subsequently 0.2 ml of allyl methyl thioether was added and the mixture was allowed to stand overnight at ambient temperature. The supernatant was decanted from the red-orange crystalline material, which was rinsed with two portions of *n*-hexane (3 ml each). Drying in vacuo yielded **3**.$(C_7H_8)_{1.5}$ (0.505 g, 0.285 mmol, 89%).

$[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2SMe][Al(Bu^t_2Al)(Bu^tAl)(Bu^tAlMe)(O_2BAr)_4](C_7H_8)_{1.5}$ (**b**): Elemental analysis for $C_{90}H_{148}O_8SB_4Al_4Zr(C_7H_8)_{1.5}$ (1770.82) found (calcd): %C = 68.31 (68.49), %H 8.97 (9.02). ^{1}H NMR (500 MHz, [D$_5$]bromobenzene, 25^{o}C): δ = 7.3 – 6.9 (m, 19.5 H; Aryl H), 3.58 (m, 6 H; C*H*$(CH_3)_2$), 3.41 (sept, ^3J(H,H) = 6.0 Hz, 1 H; C*H*$(CH_3)_2$), 3.34 (sept, ^3J(H,H) = 6.5 Hz, 1 H; C*H*$(CH_3)_2$), 2.3 (br, 1 H; C*H*(CH_3)), 2.26 (ddd, ^2J(H,H) = 10.8 Hz, ^3J(H,H) = 4.3 Hz, ^3J(H,H) = 3.3 Hz, 1 H; SC*H*$_2$), 2.14 (dd, ^2J(H,H) = 10.7 Hz, ^3J(H,H) = 12.6 Hz, 1 H; SC*H*$_2$), 1.94 (t, ^2J(H,H) = 12.9 Hz, ^3J(H,H) = 12.3 Hz, 1 H; ZrC*H*$_2$), 1.7 – 1.3 (m, CH(C*H*$_3)_2$), 1.67 (s, 3 H; SC*H*$_3$), 1.60 (s, 15 H; C_5(C*H*$_3)_5$), 1.57 (s, 15 H; C_5(C*H*$_3)_5$), 1.25 (s, 9 H; C(C*H*$_3)_3$), 1.19 (d, ^3J(H,H) = 6.6 Hz, 2 H; CH(C*H*$_3)_2$), 1.14 (s, 9 H; C(C*H*$_3)_3$), 1.09 (s, 9 H; C(C*H*$_3)_3$), 0.93 (d, ^3J(H,H) = 6.6 Hz, 2 H; CH(C*H*$_3)_2$), 0.79 (d, ^3J(H,H) = 6.2 Hz, 3 H; C(C*H*$_3$)), 0.41 (s, 9 H; C(C*H*$_3)_3$), -0.40 (s, 3 H; Al(C*H*$_3$)), -1.12 (ddd, ^2J(H,H) = 12.9 Hz, ^3J(H,H) = 6.7 Hz, ^3J(H,H) = 3.4 Hz, 1 H; ZrC*H*$_2$). ^{13}C NMR: δ =

152.6 (*o*-Ar*C*), 152.5 (*o*-Ar*C*), 152.4 (*o*-Ar*C*), 151.8 (*o*-Ar*C*), 151.6 (*o*-Ar*C*), 150.3 (*o*-Ar*C*), 149.9 (*o*-Ar*C*), 137.4 (*solv*), 130.0 (*p*-Ar*C*), 129.0 (*solv*), 128.6 (*p*-Ar*C*), 128.1 (*solv*), 127.8 (*p*-Ar*C*), 125.3 (*solv*), 124.7 ($C_5(CH_3)_5$), 124.6 ($C_5(CH_3)_5$), 121.8, (*m*-Ar*C*), 121.7 (*m*-Ar*C*), 121.5 (*m*-Ar*C*), 121.0 (*m*-Ar*C*), 120.7 (*m*-Ar*C*), 120.0 (*m*-Ar*C*), 74.0 ($ZrCH_2$), 51.4 (SCH_2), 37.9 (SCH_3), 35.6 ($CH(CH_3)_2$), 35.3 ($CH(CH_3)_2$), 34.8 ($CH(CH_3)_2$), 33.7 ($CH(CH_3)_2$), 31.6 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 30.6 ($CH(CH_3)_2$), 30.4 ($CH(CH_3)_2$), 30.0 ($CH(CH_3)_2$), 29.7 ($CH(CH_3)_2$), 29.5 ($C(CH_3)_3$), 29.0 ($CH(CH_3)_2$), 28.8 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 27.9 ($CHCH_3$), 27.0 (br; ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$), 22.5 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), 22.1 ($CH(CH_3)_2$), 21.9 ($CH(CH_3)_2$), 21.3 (*solv*), 16.8 ($CHCH_3$), 11.4 ($C_5(CH_3)_5$), 11.3 ($C_5(CH_3)_5$). ^{11}B NMR (160 MHz, [D_2]dichloromethane, 25^{o}C): δ = 28.6 ($W_{1/2}$ = 1900 Hz). ^{27}Al (130 MHz, [D_2]dichloromethane, 25^{o}C): δ = 124 (very br, $W_{1/2}$ = 35 kHz), 42.5 ($W_{1/2}$ = 3600 Hz).